Title of the Invention

Fuel Compositions

Related Applications

This application is a national phase filing under 35 U.S.C. § 371 of International Application No. PCT/EP2005/002210 which has an International filing date of March 3, 2005, and which designated the United States of America and which claims priority to German Application No. 102004011821.3, filed March 11, 2004, the entire disclosures of which are hereby incorporated herein by reference.

Field of the Invention

This invention relates generally to fuel/ethanol mixtures, and more particularly to mixtures containing additive reaction products from the reaction of di- or trialkanolamines with vegetable oils. The present invention also relates to a process for the production of diesel oil/ethanol mixtures and to the use of the reaction products as solubilizers for ethanol-containing diesel fuel.

Background Information

Numerous additives are used in hydrocarbon-based fuels, i.e. for example gas oils, heating oils, gasoline, diesel, kerosene, etc. Besides anti-corrosion and lubricity additives, known additives include flow improvers or compounds which improve the emission values of gases such as CO, CO_2 or NO_x.

International patent application **WO 98/17745** describes a preparation containing fatty acid diethanolamides, alcohol ethoxylates and fatty acid ethoxylates as additives for fuels. International patent application **WO 02/088280** describes preparations containing oleic acid alkanolamides and alkoxylated oleic acid as additives for fuels.

In International patent application **WO 02/38707**, nitrogen-containing

additives are mentioned as solubilizing aids for diesel/ethanol mixtures.

Although preparations of this type, as additives in diesel fuels, reduce gaseous emissions and can be used in low concentrations, there is still a demand for fuel additives which reduce the emission of harmful gases without adversely affecting the properties of the fuel. The use of preparations containing several components or the use of expensive raw materials and/or elaborate refining processes should be avoided on economic grounds.

Accordingly, the problem addressed by the present invention was to find an additive which, even in small quantities, would adequately reduce the emission values of harmful gases and which would be inexpensive in terms of production and raw materials. In addition, the additives would advantageously be obtainable from renewable raw materials and would represent surfactants that would enable the homogeneity of diesel fuel mixtures containing alcohols to be increased by increasing the solubility of the alcohol, particularly the commonly used ethanol, in the diesel fuel.

It has now surprisingly been found that ethanol can be adequately dissolved in fuels, preferably in diesel oil, by using reaction products of the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils.

Summary of the Invention

Briefly described, according to an aspect of the invention, a fuel composition includes: (a) at least 90% by weight of a hydrocarbon-based fuel; (b) 0.5% to 9% by weight dry ethanol; and (c) 0.1% to 5% by weight of an additive reaction product formed from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils, wherein the composition is free from alkoxylated compounds.

According to another aspect of the invention, a fuel composition

consists of (a) 90% to 98% by weight diesel oil; (b) 1% to 8% by weight dry ethanol; and (c) 0.1% to 1.5% by weight of an additive reaction product formed from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils, wherein the composition is free from alkoxylated compounds.

According to another aspect of the invention, a process for the production of diesel oil/ethanol mixtures includes adding an additive reaction product formed from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils in quantities of at most 0.1% to 5.0% by weight to dry ethanol to form a mixture, and adding the mixture to diesel oil.

In yet another aspect of the invention, a solubilizer for ethanol-containing diesel fuel includes a reaction product from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils.

Detailed Description of the Invention

Accordingly, the present invention relates firstly to fuel compositions free from alkoxylated compounds containing at least 90% by weight of a hydrocarbon-based fuel, 0.5 to 9% by weight dry ethanol and 0.1 to 5% by weight of an additive in the form of a reaction product from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils.

In the context of the present invention, fuels are understood to be any energy-yielding fuels of which the free combustion energy is converted into mechanical work. This includes all types of motor and aircraft fuels that are liquid at room temperature and normal pressure. Motor fuels, for example for automobile or truck engines, generally contain hydrocarbons, for example gasoline or higher-boiling petroleum oil fractions. The fuels according to the invention are preferably diesel oil, more particularly diesel

containing biodiesel.

Diesel fuels are obtained from gas oil by cracking or from tars obtained in the low-temperature carbonization of lignitic or hard coal. Diesel fuels are poorly flammable mixtures of liquid hydrocarbons which are used as fuels for constant-pressure or compression-ignition engines (diesel engines) and which consist predominantly of paraffins with admixtures of olefins, naphthenes and aromatic hydrocarbons. Their composition is variable and depends in particular on the method of production. Typical products have a density of 0.83 to 0.88 g/cm^3, a boiling point of 170 to 360°C and flash points of 70 to 100°C. The fuels according to the invention preferably contain diesel oil or consist of diesel oil. This also includes so-called biodiesel, i.e. a fatty acid methyl ester, preferably rapeseed oil fatty acid methyl ester, which according to the invention is preferably present in the diesel.

The dry ethanol is either commercially available "absolute ethanol" with a specific water content, which can vary according to the particular commercial product, or ethanol which is dried over generally known desiccants, such as sodium for example, to a water content of preferably below 0.5% by volume water. This drying step may optionally be followed by drying over a molecular sieve.

The fuels according to the invention are distinguished by the fact that they contain only the reaction product from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils as additives, so that there is no need for expensive mixtures of different individual substances. Accordingly, the fuel is a very inexpensive product because, apart from filtration, the reaction product does not have to be subjected to any other refinement, thus eliminating the need for expensive and time-consuming refining steps. The main reaction products from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable

oils are alkanolamides of the fatty acids present in the oils. Since, according to the invention, these alkanolamides do not have to be separated from unreacted raw materials, such as alkanolamines, partly reacted raw materials, such as di- or monoglycerides for example, other reaction products, such as glycerol or ethanol or methanol, but only have to be filtered to remove insoluble constituents, the reaction products are very cost-favorable.

A particularly preferred embodiment of the invention are fuel compositions which contain additives in the form of reaction products of di- or trialkanolamines with vegetable oils in which the vegetable oils contain fatty acid esters containing mono- or polyunsaturated C_{11-21} alkyl groups. Fatty acid esters containing monounsaturated C_{17} alkyl groups are particularly preferred.

Unsaturated representatives are, for example, lauroleic, myristoleic, palmitoleic, petroselaidic, oleic, elaidic, ricinoleic, linoleic, linolaidic, linolenic, gadoleic, arachidonic and erucic acid. Mixtures of the methyl esters of these acids are also suitable. A particularly preferred embodiment is characterized by the use of fatty acid esters containing fatty acids from the group consisting of methyl oleate, methyl palmitate, methyl stearate and/or methyl pelargonate.

The fuel compositions according to the invention preferably contain additives in the form of reaction products of di- or trialkanolamines with vegetable oils where the vegetable oils are selected from the group consisting of soybean oil, rapeseed oil, sunflower oil, peanut oil, linseed oil, olive oil, castor oil, palm oil and thistle oil. According to the invention, the reaction of soybean oil, sunflower oil or rapeseed oil, above all the reaction of soybean oil, is particularly preferred.

The vegetable oils are essentially triglyceride mixtures, the glycerol being completely esterified with relatively long-chain fatty acids.

Peanut oil contains on average (based on fatty acid) 54% by weight

oleic acid, 24% by weight linoleic acid, 1% by weight linolenic acid, 1% by weight arachic acid, 10% by weight palmitic acid and 4% by weight stearic acid. The melting point is 2 to 3°C.

Linseed oil typically contains 5% by weight palmitic acid, 4% by weight stearic acid, 22% by weight oleic acid, 17% by weight linoleic acid and 52% by weight linolenic acid. The iodine value of linseed oil is in the range from 155 to 205 and the saponification value in the range from 188 to 196. The melting point is ca. -20°C.

Olive oil mainly contains oleic acid. Palm oil contains around 2% by weight myristic acid, 42% by weight palmitic acid, 5% by weight stearic acid, 41% by weight oleic acid and 10% by weight linoleic acid as fatty acid components.

Rapeseed oil typically contains around 48% by weight erucic acid, 15% by weight oleic acid, 14% by weight linoleic acid, 8% by weight linolenic acid, 5% by weight eicosenoic acid, 3% by weight palmitic acid, 2% by weight hexadecenoic acid and 1% by weight docosadienoic acid as fatty acid components. Rapeseed oil from new plants has higher levels of the unsaturated components. Typical fatty acid contents here are 0.5% by weight erucic acid, 63% by weight oleic acid, 20% by weight linoleic acid, 9% by weight linolenic acid, 1% by weight eicosenoic acid, 4% by weight palmitic acid, 2% by weight hexadecenoic acid and 1% by weight docosadienoic acid.

80 to 85% by weight of castor oil consists of the glyceride of ricinoleic acid, around 7% by weight of the glycerides of oleic acid, 3% by weight of the glycerides of linoleic acid and around 2% by weight of the glycerides of palmitic and stearic acid.

Soybean oil contains 55 to 65% by weight, based on the total fatty acids, of polyunsaturated acids, more particularly linoleic and linolenic acid. The situation is similar with sunflower oil, of which the typical fatty acid spectrum, based on total fatty acid, is as follows: ca. 1% by weight myristic

acid, 3 to 10% by weight palmitic acid, 14 to 65% by weight oleic acid and 20 to 75% by weight linoleic acid.

All the above figures relating to the fatty acid contents of the triglycerides are known to be dependent on the quality of the raw materials and, accordingly, may vary.

In one particular embodiment of the invention, the additives are reaction products of the reaction of di- or trialkanolamines with alkyl esters of the fatty acid mixtures of the vegetable oils mentioned, particularly the preferred vegetable oils. According to the invention, the alkyl esters of the fatty acid mixtures are methyl esters and/or ethyl esters. The fatty acid composition in the mixture derives from the particular native fatty acid composition of the vegetable oil used and the particular quality of the raw material from which the methyl and/or ethyl esters are produced in known manner.

According to the invention, the di- or trialkanolamines to be reacted to form the required reaction product are alkanolamines containing C_{1-4} alkanol groups, preferably ethanolamines. The di- or trialkanolamines may have alkanol groups with the same number or with different numbers of carbon atoms. However, the reaction with amines containing two or three of the same alkanol groups is preferred, the reaction with diethanolamine or triethanolamine being particularly preferred.

The additives present in the fuel compositions according to the invention in the form of reaction products from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils are preferably characterized in that the reaction is continued until the reaction product is clear and the product dissolves clearly in diesel in the form of a 1% mixture at -10 to -20°C. In addition, apart from filtration, no other refining steps are necessary.

According to the invention, preferred fuel compositions are those in which the ratio by volume (v/v) of diesel oil to additive is in the range from

1000:0.5 to 1000:50 and preferably in the range from 1000:1 to 1000:50. A preferred embodiment is a fuel composition consisting of 90 to 98% by weight diesel oil, 1 to 8% by weight dry ethanol and 0.1 to 1.5% by weight and preferably 0.5 to 1.0% by weight of an additive in the form of the reaction product of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils.

The present invention also relates to a process for the production of diesel oil/ethanol mixtures in which either diesel oil and dry ethanol are mixed and an additive in the form of a reaction product from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils is added in quantities of at most 0.5 to 5.0% by weight or the additive in the form of a reaction product from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils is first mixed in quantities of at most 0.1 to 5.0% by weight in dry ethanol and then added to the diesel.

The use of the additives according to the invention enables mixtures of fuels with dry ethanol, preferably diesel oil with dry ethanol, to be inexpensively produced. Maximum quantities of 0.5 to 1.5% by weight of additive are preferably added to the diesel oil/ethanol mixture. The fuel composition as a whole is preferably dry, i.e. the water content of the fuel composition as a whole should be less than 0.2% by volume and preferably less than 0.1% by volume.

The additives have a solubilizing effect. Accordingly, the present invention also relates to the use of reaction products from the reaction of di- or trialkanolamines with vegetable oils or with alkyl esters of the fatty acid mixtures from vegetable oils as solubilizers for ethanol-containing diesel fuels.

Examples

Production Example 1

Reaction of soybean oil with triethanolamine (reaction ratio 1 mol oil : 1.5 mol amine):

772.4 g soybean oil and 199.3 g triethanolamine were weighed into a 2-liter three-necked flask and heated with stirring under nitrogen to 150°C. The temperature was then increased to 200°C over a period of 1 hour, followed by stirring for 4 hours at 200°C. The initially cloudy mixture turned clear after 3 hours. After the 4 hours, the mixture was cooled to 80°C and, after the addition of 0.1% filter aid, was filtered through a Seitz filter. The product was light brown, clear and liquid.

Products with other reaction ratios were similarly produced.

Production Example 2

Reaction of soybean oil with diethanolamine (reaction ratio 1 mol oil : 1.5 mol amine):

867.2 g soybean oil and 157.7 g diethanolamine were weighed into a 2-liter three-necked flask and heated with stirring under nitrogen to 160°C, followed by stirring for 3 h at that temperature. After about 2 hours, the cloudy starting mixture turned clear. After 3 hours, the mixture was cooled to 80°C and, after the addition of 0.1% filter aid, was filtered through a Seitz filter. The product was light brown, clear and liquid.

Products with other reaction ratios were similarly produced.

Production Example 3

Reaction of soybean oil fatty acid methyl ester with triethanolamine (reaction ratio 3 mol Me ester : 3 mol amine):

872.1 g soybean oil fatty acid methyl ester and 447.6 g triethanolamine were weighed into a 2-liter three-necked flask and heated with stirring under nitrogen to 190°C. The temperature was then increased

to 230°C over a period of 1 hour, followed by stirring for 3 hours at 230°C. The initially cloudy mixture turned clear after 2 hours. After the 3 hours, the mixture was cooled to 80°C and, after the addition of 0.1% filter aid, was filtered through a Seitz filter. The product was brown, clear and liquid.

Example 4

The following Table shows some physical data of the reaction products.

The effect of the additives according to the invention was tested inter alia by the cold filter plugging point test (CFPP) according to EN 116:1997. In this test, the additive-containing fuel was cooled in steps to -30°C in a mixture of 94% diesel LS, 5% ethanol and 1% reaction product, samples being taken at temperature intervals of 1°C and drawn through a standardized filter unit under a reduced pressure of 2 kPa. The temperature shown corresponds to the temperature at which the fuel is no longer able to flow through the filter unit in a fixed time.

Reaction product	Reaction ratio (equivalents) oil/methylester:DEA/TEA: ethylene glycol	AV	SV	AMV	Water (%)	Density (20°C) (g/cm³)	Pour Point (°C)
Soya methyl ester with DEA	1:1				0.08		-3
Soya methyl ester with TEA	1:1	2.9	133	134	0.26	0.960	0
Soybean oil with DEA	3:1.5	0.7	162	2.4	0.10	0.955	-6
Soybean oil with TEA	3:1.5	0.7	152	72	0.05	0.956	0
Soybean oil with TEA/ethyleneglycol	3:1:1	2.3	156	50.1	0.21	0.954	-2
Soybean oil with TEA	3:2.2	1.2	139	102		0.968	1
Soybean oil with TEA	3:0.8	0.9	171	39		0.932	-2
Soybean oil with DEA	3:2.2	5.2	146	5.2		0.967	-14
Soybean oil with DEA	3:0.8	1.1	173	4.6		0.939	-8
Soybean oil with TEA/ethyleneglycol	3:2:1	1.9	135	90		0.971	-2
Soya methyl ester with TEA/ethylene glycol	3:2:1	2.1	135	92	0.23	0.962	-3

Continuation of Table

Reaction product	Refraction (n20D)	Viscosity (40°C) mm²/s)	CFPP* (°C)	Stability in storage* 0°C	50°C	20°C	Water uptake +0.1% water
Soya methyl ester with DEA			-20	Clear	Clear	Clear	Clear
Soya methyl ester with TEA	1.4757	43.1	-23	Clear	Clear	Clear	Clear
Soybean oil with DEA	1.4808	111.0	-22	Clear	Clear	Clear	Clear
Soybean oil with TEA	1.4758	51.7	-20	Clear	Clear	Clear	Clear
Soybean oil with TEA/ethyleneglycol	1.4730	2.3	-21	Clear	Clear	Clear	Clear
Soybean oil with TEA	1.4760	61.9	-22	Clear	Clear	Clear	Clear

Soybean oil with TEA	1.4745	38.9	-21	Clear	Clear	Clear	Clear
Soybean oil with DEA	1.4826	208.0	-21	Clear	Clear	Clear	Clear
Soybean oil with DEA	1.4778	61.3	-22	Clear	Clear	Clear	Clear
Soybean oil with TEA/ethyleneglycol	1.4740	59.0	-22	Clear	Clear	Clear	Clear
Soya methyl ester with TEA/ethylene glycol	1.4735	2.1	-21	Clear	Clear	Clear	Clear

DEA = diethanolamine; TEA = triethanolamine; AV = acid value; SV = saponification value; AMV = amine value; CFPP = cold filter plugging point